PERIODIC POTENTIALS: BLOCH'S THEOREM AND THE BAND STRUCTURE OF SOLIDS

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.18.

The electron gas model of a solid ignores all interactions between particles, so we'd like to improve the model a bit by adding in some interactions. Attempting to add in any of the electric potentials explicitly results in a hideously complicated model, so we'll try something a bit simpler. In a crystal, the atoms occupy a periodic spatial structure, in the sense that if we translate the crystal rigidly along certain directions of symmetry, the structure will be transported on top of itself. We can define the three *primitive lattice vectors* $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ to be unit vectors along the three directions along which a crystal can be translated into itself. Note that these vectors are not, in general, mutually perpendicular. In a simple cubic crystal they will be perpendicular, but there are many other types of crystal structure.

In general, we can translate the crystal by an amount $\sum_{i=1}^{3} n_i \mathbf{a}_i$ where the n_is are integers, and leave the structure unchanged.

We'll also define the *reciprocal lattice vectors* $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ which have the property that $\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$. The vectors can be defined as

$$\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \tag{1}$$

with the other two defined as cyclic permutations of $\mathbf{b}_1$.

The potential function due to the fixed atoms in a crystal will have the same periodicity as the crystal structure. Therefore, if we define the translation operator $\hat{T}$ as the operator which translates the spatial coordinates by a distance $\sum_{i=1}^{3} n_i \mathbf{a}_i$, this operator commutes with the hamiltonian, since it leaves all properties of the system the same as they were before the translation. This means that any eigenfunction of the hamiltonian is also an eigenfunction of any translation operator. Suppose we have found such an eigenfunction $\psi(\mathbf{r})$. Then we can apply the specific operators $\hat{T}_i$ (which translate the coordinates by $\mathbf{a}_i$) to this function to get

$$\hat{T}_i \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{a}_i) = e^{i\theta_i} \psi(\mathbf{r}) \tag{2}$$

where the three θ_is are complex numbers independent of $\mathbf{r}$.

Now suppose we define a vector

$$\mathbf{k} \equiv \sum_{i=1}^{3} \theta_i \mathbf{b}_i \tag{3}$$

and the function

$$u(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}} \psi(\mathbf{r}) \tag{4}$$

Then, using the properties of the reciprocal lattice vectors above,

$$\begin{aligned} u(\mathbf{r}+\mathbf{a}_i) &= e^{-i\mathbf{k}\cdot(\mathbf{r}+\mathbf{a}_i)} \psi(\mathbf{r}+\mathbf{a}_i) && (5)\\ &= e^{-i\mathbf{k}\cdot\mathbf{r}} e^{-i\theta_i} e^{i\theta_i} \psi(\mathbf{r}) && (6)\\ &= e^{-i\mathbf{k}\cdot\mathbf{r}} \psi(\mathbf{r}) && (7)\\ &= u(\mathbf{r}) && (8) \end{aligned}$$

That is, u is a periodic function with the same periodicity as the crystal lattice. From its definition, this means

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r}) \tag{9}$$

This means that the wave function in a periodic potential can be written as a plane wave multiplied by a periodic function. This is known as *Bloch's theorem* after Felix Bloch, who derived it in 1928. The wave function ψ is known as a *Bloch wave*.

Studying the Bloch wave in a full three-dimensional model gets quite complex, so we'll have a look at a simplified one dimensional model. In that case, Bloch's theorem reduces to

$$\psi(x) = e^{i\theta x} u(x) \tag{10}$$

If the one dimensional 'atoms' are spaced at regular intervals of a, then

$$\begin{aligned} \psi(x+a) &= e^{i\theta a} e^{i\theta x} u(x+a) && (11)\\ &= e^{i\theta a} e^{i\theta x} u(x) && (12)\\ &= e^{i\theta a} \psi(x) && (13) \end{aligned}$$

Now comes a bit of a fudge. Any real solid, of course, isn't completely invariant under translation since it has finite boundaries, and shifting the crystal by a certain amount is going to push some atoms out into empty

space so they don't lie on top of previous atomic positions. The fudge is to wrap the solid into a loop so that the two edges (remember we're using only one dimension) meet. If the total number of atoms in the loop is N, then we must have

$$\psi(x+Na) = \psi(x) = e^{i\theta Na}\psi(x) \tag{14}$$

This means that $e^{i\theta Na} = 1$, so

$$\theta = \frac{2\pi n}{Na} \tag{15}$$

for some integer n.

So far all we've said about the potential is that it's periodic; we haven't said what form it takes. We could use a series of square wells or other potentials with a finite width, but to illustrate one of the most important properties of a periodic potential, we can use a series of delta functions. We've already worked out the math involved in the delta function wave functions, so we can adapt that here. If we take the delta functions to be pointing upwards instead of downwards, we eliminate the bound state which makes the calculation a bit easier. Remember, all we're really trying to do is see what effect a periodic potential has, so the precise form of the potential isn't important here (although obviously if we're trying to create a more realistic model of a crystal, it is!). So we'll take as our potential

$$V(x) = \alpha \sum_{i=1}^{N-1} \delta(x - ia) \tag{16}$$

where α is a positive constant. Because of Bloch's theorem, we need to find the wave function only within one period of the potential, since the recursion relation allows us to find the wave function everywhere else from that.

In between delta functions, the Schrödinger equation is just

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{17}$$

which has the usual solution for $0 < x < a$

$$\psi(x) = A\sin(kx) + B\cos(kx) \tag{18}$$

where $k^2 = 2mE/\hbar^2$. Applying Bloch's theorem, the wave function in the

cell immediately to the left of the origin (that is, if we shift x by a distance $-a$) is

$$\psi(x-a) = e^{-i\theta a}\left[A\sin(kx) + B\cos(kx)\right] \tag{19}$$

where $0 < x < a$, or, to write this as an equation for $\psi(x)$:

$$\psi(x) = e^{-i\theta a}\left[A\sin(k(x+a)) + B\cos(k(x+a))\right] \tag{20}$$

At the delta function boundary at $x = 0$, the wave function must be continuous, so

$$B = e^{-i\theta a}\left[A\sin(ka) + B\cos(ka)\right] \tag{21}$$

Because the delta function is infinite, the derivative of ψ is *not* continuous, but we can use the same trick we used earlier to get a boundary condition here. The difference in the derivative across the boundary is

$$\Delta\psi'(0) = \frac{2m\alpha}{\hbar^2}\psi(0) \tag{22}$$

$$= \frac{2m\alpha}{\hbar^2}B \tag{23}$$

The derivative on the right is, at $x = 0$

$$\psi'_+(0) = kA \tag{24}$$

and on the left:

$$\psi'_-(0) = ke^{-i\theta a}\left[A\cos ka - B\sin ka\right] \tag{25}$$

Therefore

$$kA - ke^{-i\theta a}\left[A\cos ka - B\sin ka\right] = \frac{2m\alpha}{\hbar^2}B \tag{26}$$

From 21

$$A = \frac{e^{i\theta a} - \cos(ka)}{\sin(ka)}B \tag{27}$$

We can substitute this into 26:

$$\frac{e^{i\theta a}-\cos(ka)}{\sin(ka)}kB - kBe^{-i\theta a}\left[\frac{e^{i\theta a}-\cos(ka)}{\sin(ka)}\cos(ka)-\sin(ka)\right] = \frac{2m\alpha}{\hbar^2}B \tag{28}$$

$$e^{i\theta a}-\cos(ka)-\left(\cos(ka)-e^{-i\theta a}\cos^2(ka)-e^{-i\theta a}\sin^2(ka)\right) = \frac{2m\alpha}{\hbar^2 k}\sin(ka) \tag{29}$$

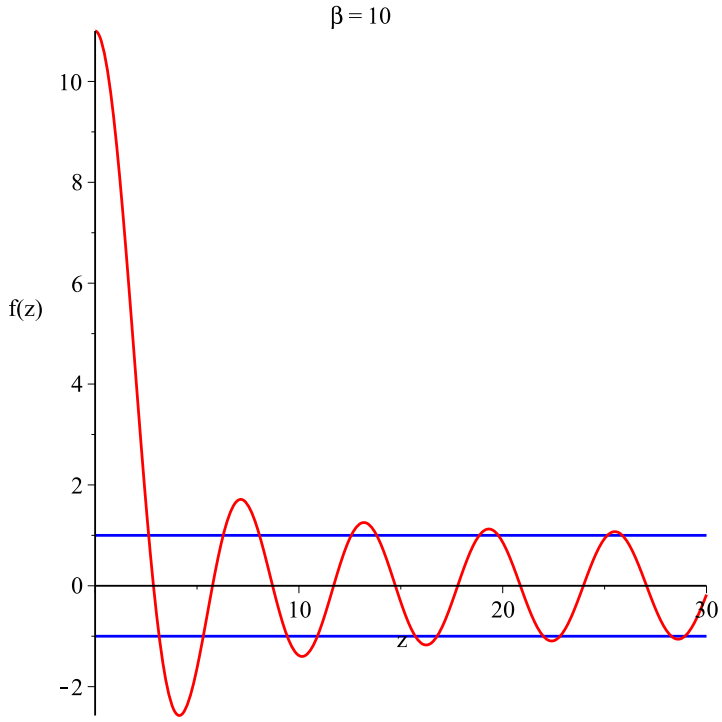
$$e^{i\theta a}+e^{-i\theta a}-2\cos(ka) = \frac{2m\alpha}{\hbar^2 k}\sin(ka) \tag{30}$$

$$\cos(\theta a) = \frac{m\alpha}{\hbar^2 k}\sin(ka)+\cos(ka) \tag{31}$$

If we define $z \equiv ka$ and $\beta \equiv m\alpha a/\hbar^2$ then the RHS of this is a function of z:

$$\frac{m\alpha}{\hbar^2 k}\sin(ka)+\cos(ka) = \beta\frac{\sin z}{z}+\cos z \equiv f(z) \tag{32}$$

In order for $\cos(\theta a)$ to be real, $-1 \leq f(z) \leq 1$ must hold. However, for most values of β there will be regions where $f(z) > 1$. A plot shows these regions better:



The blue lines show the limits within which $\cos(\theta a) \leq 1$, so it is only for these values of z that solutions exist. These regions are known as *bands* and the gaps between them are known as, well, *gaps*. Because $\theta = \frac{2\pi n}{Na}$ and N is huge, there are a huge number of possible states within each band. Working out the energy of a given state requires specifying the value of $\theta a = 2\pi n/N$ and then solving the transcendental equation for k, which has to be done graphically or numerically.

Instead of solving for A in terms of B as we did above, we can instead write B in terms of A:

$$B = \frac{\sin ka}{e^{i\theta a} - \cos ka} A \tag{33}$$

Substituting this into 18 we get

$$\psi(x) = A\sin kx + A\frac{\sin ka\cos kx}{e^{i\theta a} - \cos ka} \tag{34}$$

$$\left(e^{i\theta a} - \cos ka\right)\psi(x) = A\sin kx\left(e^{i\theta a} - \cos ka\right) + A\sin ka\cos kx \tag{35}$$

$$= Ae^{i\theta a}\sin kx + A\sin k(a-x) \tag{36}$$

$$\left(1 - e^{-i\theta a}\cos ka\right)\psi(x) = A\sin kx + Ae^{-i\theta a}\sin k(a-x) \tag{37}$$

$$\psi(x) = \frac{A}{1 - e^{-i\theta a}\cos ka}\left(\sin kx + e^{-i\theta a}\sin k(a-x)\right) \tag{38}$$

$$\equiv C\left(\sin kx + e^{-i\theta a}\sin k(a-x)\right) \tag{39}$$

where

$$C = \frac{A}{1 - e^{-i\theta a}\cos ka} \tag{40}$$

There is a problem with this wave function for the special case where $z = ka = n\pi$, which occurs at the top of each band (since $f(z) = (-1)^n$ there). In that case, 31 and 32 give us

$$\cos(\theta a) = \frac{\beta}{n\pi}\sin(n\pi) + \cos(n\pi) \tag{41}$$

$$= 0 + (-1)^n \tag{42}$$

$$= (-1)^n \tag{43}$$

Since $|\cos(\theta a)| = 1$, we must have $\sin(\theta a) = 0$, which means $e^{i\theta a} = e^{-i\theta a} = \cos(\theta a) = (-1)^n = \cos(ka)$ and 33 involves the indeterminate ratio 0/0.

We can resolve this problem by returning to 26, which now becomes

$$kA - ke^{-i\theta a}\left[A\cos ka - B\sin ka\right] = \frac{2m\alpha}{\hbar^2}B \tag{44}$$

$$kA - (-1)^n k\left[(-1)^n A - 0\times B\right] = \frac{2m\alpha}{\hbar^2}B \tag{45}$$

$$0 = \frac{2m\alpha}{\hbar^2}B \tag{46}$$

$$B = 0 \tag{47}$$

The wave function in this case must then be

$$\psi(x) = A \sin kx \tag{48}$$

At each delta function there is now no discontinuity in the derivative since

$$\Delta\psi'(0) = \frac{2m\alpha}{\hbar^2}\psi(0) = 0 \tag{49}$$

Because the wave function itself is zero at the one point where the potential (the delta function) is non-zero, the potential is effectively invisible in this case.

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